

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-272714

(43)Date of publication of application : 21.10.1997

(51)Int.Cl.

C08F 8/00
C08F 8/42
C08F299/00
C08L 83/04
// C08F 20/12

(21)Application number : 08-326475

(71)Applicant : KANEGAFUCHI CHEM IND CO LTD

(22)Date of filing : 06.12.1996

(72)Inventor : KUSAKABE MASATO
KITANO KENICHI

(30)Priority

Priority number : 08 22233 Priority date : 08.02.1996 Priority country : JP

(54) PRODUCTION OF (METH)ACRYLIC POLYMER HAVING TERMINAL FUNCTIONAL GROUP

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a process for producing a (meth)acrylic polymer having a large amount of terminal crosslinkable functional groups such as alkenyl or crosslinkable silyl groups and to provide a curable composition comprising the same.

SOLUTION: An initiator comprising an organic halide or halogenated sulfonyl compound and a catalyst comprising a metal complex having as the central metal an element belonging to Group 8, 9, 10, or 11 or the Periodic Table are used for polymerization to obtain a (meth)acrylic polymer having a terminal structure represented by the formula $-\text{CH}_2-\text{C}(\text{R}_1)(\text{CO}_2\text{R}_2)(\text{X})$ (R_1 is hydrogen or methyl; R_2 is a 1-20C alkyl, aryl, or aralkyl; and X is chloride, bromine, or iodine). The halogen atoms of the polymer are replaced with substituents each having an alkenyl or crosslinkable silyl group to obtain the target polymer.

* NOTICES *

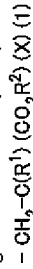
JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. *** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

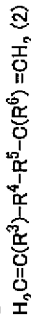
[Claim 1] An organic halogenated compound or a sulfonyl halide compound. An initiator, the 8th fellows of the periodic table, are obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. A manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta) changing into an alkenyl group content substituent halogen of an acrylic polymer which has terminal structures shown by the general formula 1 (meta).



(As for hydrogen or a methyl group, and R^2 , in inside of formula, and R^1 , an alkyl group of 1-20, an aryl group or an alkyl group, and X are [a carbon number] chlorine, bromine, or iodine)

[Claim 2] An organic halogenated compound or a sulfonyl halide compound. An initiator, the 8th fellows of the periodic table, An acrylic polymer which has terminal structures which show nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. The manufacturing method according to claim 1 making a compound having an alkenyl group of polymerization nature, and other at least one alkenyl group react.

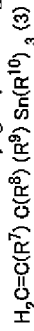
[Claim 3] The manufacturing method according to claim 2 which is a compound in which a compound having an alkenyl group of polymerization nature and other at least one alkenyl group is shown by the general formula 2.



(As for R^3 and R^6 , -C(O) O- (ester group) or o-, m-, p-phenylene group, and R^5 may include one or more ether bonds among a formula by a divalent organic group of direct coupling or the carbon numbers 1-20, as for hydrogen or methyl, and R^4)

[Claim 4] The manufacturing method according to claim 1 making an organic metallic compound which has an alkenyl group react to an acrylic polymer which has terminal structures shown by the general formula 1 (meta).

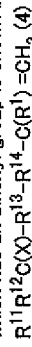
[Claim 5] The manufacturing method according to claim 4, wherein an organic metallic compound which has an alkenyl group is an organic tin compound shown by the general formula 3.



among a formula, R^7 , R^8 , and R^9 may be mutually the same at hydrogen or an alkyl group of the carbon numbers 1-10, an aryl group, or an alkyl group, or may differ from each other. R^{10} is an alkyl group of the carbon numbers 1-10, an aryl group, or an alkyl group.

[Claim 6] The manufacturing method according to claim 1 to 5, wherein an organic halogenated compound which is an initiator, or a sulfonyl halide compound is a halogenide which has an alkenyl group.

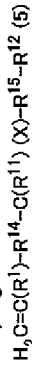
[Claim 7] The manufacturing method according to claim 6 which is a compound in which a halogenide which has an alkenyl group is shown by the general formula 4 or 5.



inside of formula, and R^1 — hydrogen or a methyl group, R^{11} and R^{12} — hydrogen. Or a univalent alkyl group of the carbon numbers 1-20, an aryl group, an alkyl group or a thing mutually connected

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi?atw_u=http://www4.ipdl.inpit.go.jp... 2010/03/03

in the other end, and R^{13} , -X in which C(O) O- (ester group), -C(O)- (keto group) or o-, m-, p-phenylene group, and R^{14} may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1-20 is chlorine, bromine, or iodine.



(a formula — inside — R — one — R — 11 — R — 12 — R — 14 — X — the above — the same — R — 15 — direct coupling — C — (— O —) — O — (ester group) — C(O)— (keto group) or o-, m-, and p-phenylene group)

[Claim 8] An acrylic polymer which has the structure which is shown to one end by alkenyl group and shown in other ends by the general formula 1 by a method of claim 6 or 7 (meta) is manufactured. A manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta) characterized by carrying out coupling of the halogen ends using a compound which can furthermore replace halogen of the general formula 1, and which has a total of two or more same or different functional groups.

[Claim 9] The manufacturing method according to claim 8 performing a coupling reaction of the halogen ends of the general formula 1 using a compound chosen from a group which consists of polyol, polyamine, polycarboxylic acid, polythiol and those salts, and an alkaline metal sulfide.

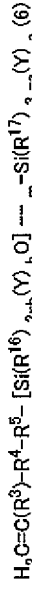
[Claim 10] (A) an acrylic polymer which has an alkenyl group at the end obtained by one method of claims 1-9 (meta-), and a hardenability constituent containing (B) hydrosilyl group content compound.

[Claim 11] (A) The hardenability constituent according to claim 10 which has a molecular weight of an acrylic polymer which has an alkenyl group at the end of an ingredient (meta) in the range of 500-50000.

[Claim 12] An organic halogenated compound or a sulfonyl halide compound. An initiator, the 8th fellows of the periodic table, are obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) changing into a crosslinkable-silyl-groups content substituent halogen of an acrylic polymer which has terminal structures shown by the general formula 1 (meta).

[Claim 13] An organic halogenated compound or a sulfonyl halide compound. An initiator, the 8th fellows of the periodic table, An acrylic polymer in which nine fellows, ten fellows, or 11 group elements are shown by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. The manufacturing method according to claim 12 making a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature react.

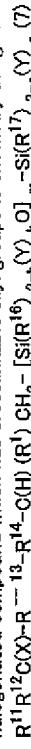
[Claim 14] The manufacturing method according to claim 13 whose compound having an alkenyl group and crosslinkable silyl groups of polymerization nature is a compound shown by the general formula 6.



(R^3 , R^4 , and R^5 among a formula) R^3 in the general formula 2, R^4 , and R^5 — the same — R^{16} and R^{17} . All An alkyl group of the carbon numbers 1-20, an aryl group, an alkyl group, or (R') $_{3-b}$ — (R') is a univalent hydrocarbon group of the carbon numbers 1-20, and three R' being the same and differing — **** — when the Tori ORGANO siloxy group shown is shown and R^{16} or two or more R^{17} exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is an integer of 0-19. However, it shall satisfy that it is $a+b \geq 1$.

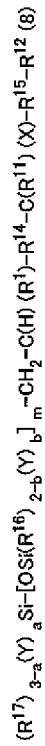
[Claim 15] The manufacturing method according to claim 12 to 14 which is an organic halogenated compound which is an initiator, or a halogenide in which a sulfonyl halide compound has crosslinkable silyl groups.

[Claim 16] The manufacturing method according to claim 15 which is a compound in which an organic halogenated compound which has crosslinkable silyl groups is shown by the general formula 7 or 8.



(The inside of a formula, R^1 , R^{11} , R^{12} , R^{13} , R^{14} , R^{16} , R^{17} , a, b, m, X, and Y are the same as the above)

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi?atw_u=http://www4.ipdl.inpit.go.jp... 2010/03/03



(The inside of a formula R^1 , R^{11} , R^{12} , R^{14} , R^{15} , R^{16} , R^{17} , a, b, m, X, and Y are the same as the above)
 [Claim 17]An acrylic polymer which has the structure which is shown to one end by crosslinkable silyl groups, and is shown in other ends by the general formula 1 by a method of claim 15 or 16 (meta) is manufactured, A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) characterized by carrying out coupling of the halogen ends using a compound which can furthermore replace halogen of the general formula 1, and which has a total of two or more same or different functional groups.

[Claim 18]The manufacturing method according to claim 17 performing a coupling reaction of the halogen ends of the general formula 1 using a compound chosen from a group which consists of polyol, polyamine, polycarboxylic acid, polythiol and those salts, and an alkaline metal sulfide.

[Claim 19]A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) making hydrosilane which has crosslinkable silyl groups add to an acrylic polymer which has an alkenyl group at the end obtained by one method of claims 1-9 (meta).

[Claim 20]A hardenability constituent which uses as the main ingredients an acrylic polymer which is obtained by one of methods according to claim 12 to 19, and which has crosslinkable silyl groups at the end (meta).

[Claim 21]The hardenability constituent according to claim 20 which has a molecular weight of an acrylic polymer which has crosslinkable silyl groups at the end (meta) in the range of 500-50000.

[Translation done.]

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Field of the Invention] This invention relates to the hardenability constituent which used for the end of the manufacturing method of a functional group and the acrylic polymer which specifically has an alkenyl group or crosslinkable silyl groups (meta), and this polymer.

[0002] [Description of the Prior Art] The polymer which has a functional group at the end constructs a bridge by combining with a very thing independent or a suitable hardening agent, and giving the hardened material which was excellent in heat resistance, endurance, etc. is known. The polymers which have an alkenyl group or crosslinkable silyl groups at the end especially are those examples of representation. The polymer which has an alkenyl group at the end carries out bridge construction hardening using a hydrosilyl group content compound as a hardening agent, or by using the photocrosslinking reaction. The polymer which has crosslinkable silyl groups at the end gives a hardened material by absorbing hygroscopic surface moisture under existence of a suitable condensation catalyst.

[0003] As a principal chain skeleton of the polymer which it has at the end, such an alkenyl group or crosslinkable silyl groups, Polyether system polymers, such as polyethylene oxide, polypropylene oxide, polytetramethylene oxide, Hydrocarbon system polymers, such as polybutadiene, polyisoprene, polychloroprene, polyisobutylenes, or those hydrogenation things, Polyester system polymers, such as polyethylene terephthalate, polybutylene terephthalate, and polycaprolactone, etc. are illustrated, and it is used for various uses based on a principal chain skeleton and bridge construction form.

[0004] [Problem(s) to be Solved by the Invention] What has a functional group at the end with the polymer of a vinyl system obtained by a radical polymerization by one side of the polymer which was illustrated above, and which is obtained by ionic polymerization or condensation polymerization has hardly been put in practical use yet. Also in a vinyl system polymer, an acrylic (meta) polymer, it has the characteristics which are not obtained in an above-mentioned polyether system polymer, hydrocarbon system polymer, or polyester system polymer, such as high weatherability and transparency, and what has an alkenyl group and crosslinkable silyl groups in a side chain is used for the high weatherability paint etc.

[0005] If the acrylic polymer which has an alkenyl group or crosslinkable silyl groups in molecular chain terminals (meta) can be obtained by a simple method, the hardened material which excelled [side chain] in hardened material physical properties as compared with what has a cross-linking group can be obtained. Therefore, although the manufacturing method has been examined by the researcher of the former many, it is not easy to manufacture them industrially.

[0006] Use alkenyl group content disulfide for JP,5-255415,A as a chain transfer agent. The synthetic method of the acrylic polymer which has an alkenyl group in both ends (meta) again to JP,5-262808,A. Although the acrylic polymer which has hydroxyl in both ends (meta) is compounded using the disulfide which has hydroxyl and the synthetic method of the acrylic polymer which has an alkenyl group in both ends further using the reactivity of hydroxyl (meta) is indicated, it is not easy to introduce an alkenyl group into both ends certainly by these methods. On the other hand to JP,59-16801,4,A, the manufacturing method of the acrylic polymer which has crosslinkable silyl groups as a chain transfer agent in the both ends using the disulfide compound which has crosslinkable silyl groups (meta). Although the manufacturing method of the acrylic polymer which has crosslinkable silyl

groups in both ends (meta) by using for JP,61-133201,A the hydrosilane which has crosslinkable silyl groups, and halogenation Silang is indicated. In these methods, it is difficult to introduce crosslinkable silyl groups into both ends certainly, and the hardened material which has the satisfactory characteristic cannot be obtained. In order to introduce a functional group into an end certainly, a chain transfer agent must be used in large quantities, and it is a manufacturing process top problem. [0007] Therefore, let it be SUBJECT to provide the manufacturing method of the acrylic polymer which has an alkenyl group or crosslinkable silyl groups by a high ratio at the end as compared with the conventional method (meta), and the hardenability constituent using them in this invention. [0008]

[Means for Solving the Problem] An acrylic polymer which has an alkenyl group at the end among aforementioned problems (meta). An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, it is obtained by changing into an alkenyl group content substituent halogen of an acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst.



(As for hydrogen or a methyl group, and R^2 , in inside of formula, and R^1 , an alkyl group of 1-20, an aryl group or an aralkyl group, and X are [a carbon number] chlorine, bromine, or iodine) As an example of such a manufacturing method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has the structure which shows the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. A method of making an organic metallic compound which has an alkenyl group react to an acrylic polymer which has a method to which a compound having an alkenyl group of polymerization nature and other at least one alkenyl group is made to react, or terminal structures shown by the general formula 1 (meta), etc. are mentioned. A halogenide which has an alkenyl group, or a sulfonyl halide compound is used as an initiator. An acrylic polymer which has an alkenyl group at the end (meta) can be obtained also by manufacturing an acrylic polymer which has an alkenyl group in one end and has the structure of the formula 1 at other ends (meta), and changing halogen of the end into an alkenyl group content substituent.

[0009] An acrylic polymer which is obtained by such a method and which has an alkenyl group at the end (meta) is used for an acrylic polymer which has an alkenyl group at the (A) end (meta), and a hardenability constituent containing (B) hydrosilyl group content compound. An acrylic polymer which has crosslinkable silyl groups at the end (meta). An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, it can manufacture by changing into a crosslinkable-silyl-groups content substituent halogen of an acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. As an example of such a manufacturing method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has terminal structures which show the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. A method to which a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature is made to react is mentioned. A halogenide which has crosslinkable silyl groups is used as an initiator. It can obtain also by manufacturing an acrylic polymer which has crosslinkable silyl groups in one end, and has the structure shown in other ends by the formula 1 (meta), and changing halogen of the end into a crosslinkable-silyl-groups content substituent further.

[0010] An acrylic polymer which has crosslinkable silyl groups at the end (meta) can be manufactured also by making hydrosilane which has crosslinkable silyl groups add to an acrylic polymer which has an alkenyl group at the end (meta). Thus, an acrylic polymer which has crosslinkable silyl groups at the end obtained (meta) can be used as a hardenability constituent.

[0011] It also has the feature that an acrylic polymer which has a functional group of cross-linking at the end obtained by this invention (meta) has narrow molecular weight distribution.

[0012]

[Embodiment of the Invention] First, the manufacturing method of the acrylic polymer which has an alkenyl group at the end (meta). An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. The halogen of the acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by the polymerization method using the metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst is changed into an alkenyl group content substituent.



(As for hydrogen or a methyl group, and R^2 , in inside of formula, and R^1 , the alkyl group of 1-20, an aryl group or an aralkyl group, and X are [a carbon number] chlorine, bromine, or iodine) The method of using a carbon tetrachloride, carbon tetrabromide, a methylene chloride, a methylene bromide, etc. for an end in the polymerization which uses a halogenide as a chain transfer agent (TEROGEN) as a manufacturing method of the acrylic polymer which has halogen (meta) is used. However, it is difficult to introduce halogen into both ends certainly by this method.

[0013] If the living radical polymerization studied energetically these days is used to this method, halogen is introduced into an end by a high ratio (Matyjaszewski et al. [for example,] J. Refer to Am.Chem.Soc.1995, 117 and 5614, Macromolecules 1995, 28, and 7901, Science 1996, 272, and 866 or Sawamoto et al., and Macromolecules 1995, 28, and 1721. Though these methods are radical polymerizations, a polymerization advances in living, the narrow ($\text{Mw}/\text{Mn}=1.1-1.5$) polymer of molecular weight distribution is obtained, and a molecular weight can be freely controlled by the preparation ratio of a monomer and an initiator.

[0014] The organic halogenated compound which has an organic halogenated compound and a carbon-halogen bond with especially high reactivity in this living radical polymerization. (For example, the ester compound which has halogen in an alpha position and the compound which has halogen in a benzylic position), or a sulfonyl halide compound is used as an initiator. As a catalyst, the metal complex which uses the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal is used. As a metal kind, univalent copper, a divalent ruthenium, and divalent iron are especially preferred. If it illustrates concretely, they will be a cuprous chloride, the first copper of bromination, a cuprous iodide, a cuprous cyanide, copper I oxide, the first copper of acetic acid, the first copper of perchloric acid, etc. When using a copper compound, in order to improve catalytic activity, ligands, such as a 2,2'-bipyridyl and its derivative, a 1,10-phenanthroline, and its derivative, are added. The tris(phenyl) phosphine complex ($\text{RuCl}_2(\text{PPh}_3)_3$) of ruthenium chloride of bivalence is also preferred as a catalyst. When using this catalyst, in order to improve that activity --- doria --- aluminum compounds, such as RUKOKI sial minium, are added. The tris(phenyl) phosphine complex ($\text{FeCl}_2(\text{PPh}_3)_3$) of the ferric chloride of bivalence is also preferred as a catalyst.

[0015] In order to obtain the acrylic (meta) polymer of cross-linking using this polymerizing method, the organic halogenated compound which has the two or more starting points, or a sulfonyl halide compound is used as an initiator. If it illustrates concretely, σ^- , m^- , p^- - $\text{XCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{X}$, σ^- , m^- , p^- - $\text{CH}_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_4-\text{CH}(\text{X})-\text{C}_6\text{H}_4-\text{C}(\text{X})(\text{X})-\text{C}_6\text{H}_4-\text{CH}_2\text{X}$ (however, inside of upper chemical formula, and C_6H_4 a phenylene group and X chlorine, bromine, or iodine), $\text{RO}_2\text{C}-\text{C}(\text{H})(\text{X})-\text{CH}_2-\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $\text{RO}_2\text{C}-\text{C}(\text{H})(\text{X})-\text{CH}_2-\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $\text{RC}(\text{O})-\text{C}(\text{H})(\text{X})-\text{CH}_2-\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{R}$, $\text{RC}(\text{O})-\text{C}(\text{H})(\text{X})-\text{CH}_2-\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{R}$ (as for the alkyl group of the carbon numbers 1-20, an aryl group or an aralkyl group, and n, in the inside of a formula, and R, the integer of 0-20 and X are chlorine, bromine, or iodine).

$\text{XCH}_2\text{C}(\text{O})\text{CH}_2\text{X}$ and $\text{CH}_3\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{C}(\text{H})(\text{X})\text{CH}_3$ (CH_3)₂ $\text{C}(\text{X})\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{X})(\text{CH}_3)_2$ (as for the inside of the upper formula, and X, chlorine, bromine or iodine, and n are the integers of 0-20), $\text{XCH}_2\text{CO}_2-\text{CH}_2-\text{CO}_2\text{CH}_2\text{X}$, $\text{CH}_3\text{C}(\text{H})(\text{X})\text{CO}_2-\text{CH}_2-\text{OCOC}(\text{H})(\text{X})\text{CH}_3$ (CH_3)₂ $\text{C}(\text{X})\text{CO}_2-\text{CH}_2-\text{OCOC}(\text{X})(\text{CH}_3)_2$ (as for the inside of the upper formula, and X, chlorine, bromine, iodine, and n are the integers of 0-20), $\text{XCH}_2\text{C}(\text{O})\text{C}(\text{O})\text{CH}_2\text{X}$ and $\text{CH}_3\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{X})(\text{CH}_3)_2$

2^- , σ^- , m^- , p^- - $\text{XCH}_2\text{CO}_2-\text{C}_6\text{H}_4-\text{OCOC}(\text{H})(\text{X})\text{CH}_3$, σ^- , m^- , p^- - $\text{CH}_3\text{C}(\text{H})(\text{X})\text{CO}_2-\text{C}_6\text{H}_4-\text{OCOC}(\text{H})(\text{X})\text{CH}_3$, σ^- , m^- , p^- - $(\text{CH}_3)_2\text{C}(\text{X})\text{CO}_2-\text{C}_6\text{H}_4-\text{OCOC}(\text{X})(\text{CH}_3)_2$, σ^- , m^- , p^- - $\text{XSO}_2-\text{C}_6\text{H}_4-\text{SO}_2\text{X}$ (the inside of the upper formula and X are chlorine, bromine, or iodine), ** is mentioned.

[0016] As an acrylic monomer used in this polymerization (meta), there are no restrictions in particular and various kinds of things can be used. If it illustrates, methyl acrylate (meta), ethyl acrylate (meta), (Meta) Acrylic acid-n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-n-pentyl, (Meta) Acrylic acid-n-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-n-heptyl, acrylic acid (meta)-n-octyl, (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) They are acrylic acid toluyl, acrylic acid (meta)-2-hydroxyethyl, acrylic acid (meta)-2-methoxyethyl, acrylic acid (meta)-3-methoxy butyl, acrylic acid (meta)-2-hydroxyethyl, acrylic acid (meta)-2-hydroxypropyl, etc. Even if it uses these independently and they mix and use two or more sorts, they are not cared about. Carrying out copolymerization of other vinyl system monomers, such as styrene, alpha-methylstyrene, acrylonitrile, if needed does not interfere at all.

[0017] A polymerization can be performed in a non-solvent or various kinds of solvents. A polymerization can be performed in room temperature -200 **, and it is 50-150 ** preferably. The acrylic polymer which has an alkenyl group at the end (meta) can be obtained by changing halogen of the acrylic polymer which is obtained by the above-mentioned polymerization and which has halogen at the end (meta).

[0018] As such a method, first, the acrylic polymer which has terminal structures shown by the general formula 1 by the above-mentioned polymerization (meta) is manufactured, and the method to which the compound it has a compound and an alkenyl group of polymerization nature and other at least one alkenyl group further is made to react as the 2nd monomer is mentioned. In the above-mentioned polymerization, the polymerization end holds polymerization activity, and if a vinyl system monomer is newly added, a polymerization will advance again. Therefore, if the vinyl system monomer having the alkenyl group of polymerization nature and other at least one alkenyl group is added, A radical addition reaction occurs in a polymerization activity alkenyl group portion, other alkenyl groups remain, while it has been unreacted, and the acrylic polymer which has an alkenyl group at the end (meta) is obtained. After the 1st polymerization is completed and it isolates a polymer, it may add with a catalyst and such 2nd monomer may be made to newly react, and it may add in the middle of a polymerization (inch-situ), and it may be made to react. In the case of the latter, the monomer inversion rate of the 1st polymerization is so good that it is high, and is not less than 80% preferably. An alkenyl group will be distributed over the side chain instead of a molecular terminal as it is 80% or less, and the mechanical characteristic of a hardened material will be spoiled.

[0019] Under the present circumstances, the compound having the alkenyl group of such polymerization nature, and other at least one alkenyl group, if a quantity equal to the number of polymerization ends (it is almost equal to the number of the starting points of an initiator since it is living polymerization) is added, one alkenyl group will be theoretically introduced into all the ends at a time, but. In order to introduce an alkenyl group into a whole end certainly, specifically, it is good to use one to 5 times to the number of ends in excessive amount. If it uses more mostly than 5 times, an alkenyl group will be introduced into the end of a polymer by high density, and it is not desirable on hardened material physical properties.

[0020] Although there is no restriction in particular as a compound having the alkenyl group of polymerization nature, and other at least one alkenyl group, it is general formula $2\text{H}_2\text{C}=\text{C}(\text{R}^3)-\text{R}^4-\text{R}^5-\text{C}(\text{R}^6)=\text{CH}_2$ (2), for example.

the inside of a formula, R^3 and R^6 --- hydrogen or methyl, and R^4 - $\text{C}(\text{O})\text{O}$ - (ester group). Or σ^- , m^- , p-phenylene group, and R^5 may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20. The compound shown is mentioned. As for the thing of an ester coupling, R^4 is [an acrylate (meta) system compound and R^4 of the thing of a phenylene group] the compounds of a styrene system. As R^5 in the general formula 2, alkylene groups, such as methylene, ethylene, and propylene, An alkylene group including ether bonds, such as aralkyl group [

such as *o*-, *m*-, *p*-phenylene group, and benzyl,] and $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-$ and $-\text{O}-\text{CH}_2-$, are

illustrated.

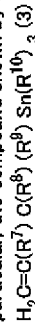
[0021]H from the point that acquisition is easy also in these $\text{---}_2\text{C}=\text{CC}(\text{H})\text{---}(\text{O})\text{C}(\text{CH}_2)_n\text{---CH}=\text{CH}_2$ and $\text{H---}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{C}(\text{CH}_2)_n\text{---CH}=\text{CH}_2$ (in each of above-mentioned formulas, n is an integer of 0-20).

[illegible]

**** — it is desirable.**

[0022] If it is considered as the method of introducing an alkenyl group into an end, various kinds of organic metallic compounds which have an alkenyl group can be made to be able to act on the end shown by the formula 1 to the polymer which has halogen, and the method of replacing halogen directly can also be used. As such an organic metallic compound, organic lithium, organic sodium, organic potassium, organic magnesium, organic tin, organic zinc, organic copper, etc. are mentioned. Organic tin and an organocopper compound are preferred at the point that react especially to halogen of the formula 1 selectively, and reactivity with a carbonyl group is low.

[0023] As an organic tin compound which has an alkenyl group, although there is no restriction in particular, the compound shown by the general formula 3 is preferred.



among the formula, R⁷, R⁸, and R⁹ may be mutually the same at hydrogen or the alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group, or may differ from each other. R¹⁰ is an alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group.

If the example of the organic tin compound of the formula 3 is shown, allyl tributyl tin, allyl trimethyl tin, ant RUTORI (*n*-octyl) tin, ant RUTORI (cyclohexyl) tin, etc. will be illustrated. The alkenyl group content organic tin compound shown by the general formula 3, it may add in the middle of the polymerization of an acrylic system monomer (meta), and the acrylic polymer which has terminal structures of the general formula 1 (meta) may be made to react anew, since it reacts to end halogen of the general formula 1 by a radical mechanism once it isolates. In the case of the latter, a reaction advances only with heating, but in order to promote a reaction, radical initiators, such as azobisisobutyronitrile, may be added.

[0243]As an organocopper compound which has an alkenyl group, divinyl copper lithium, diaryl copper lithium, diisopropenyl copper lithium, etc. are illustrated. As a converting method to the alkenyl group of an end halogen group, it is also possible to use the method of making it react to the electrophilicity of a compound which makes a metal simple substance or an organic metallic compound act, metalizes halogen to the acrylic polymer which has halogen at the end (meta), and has an alkenyl group after an appropriate time.

[2025]As a metal simple substance, alkaline-earth metals, such as alkaline metals, such as lithium, sodium, and potassium, magnesium, and calcium, aluminum, zinc, etc. are mentioned. The point that a side reaction which the metal-ized portion (eno rate anion) attacks other ester groups among these, or it transfers does not occur easily to especially zinc is preferred. As an example of an organic metallic compound, organic magnesium, such as organic lithium, organic sodium, organic potassium, and a Grignard reacting agent, organic aluminum, an organozinc compound, etc. are mentioned. In order to make halogen metal-ize efficiently, it is preferred to use organic lithium and organic magnesium.

http://www4.ipdl.inp.it/go.jp/cgi-bin/tran_web.cgi/eije?atw_u=http%3A%2F%2Fwww4.ipdl.i...

[0026] Various kinds of things can be used as an electrophilicity compound which has an alkanyl group. For example, they are an alkanyl group content compound which has a leaving group like halogen or an acetyl group, a carbonyl compound which has an alkanyl group, an isocyanate compound which has an alkanyl group, the acid halide which has an alkanyl group, etc. If the alkanyl group content compound which has a leaving group like halogen or an acetyl group among these is used, since a hetero atom will not be introduced into a main chain and the weatherability which is the original feature of an acrylic (meta) polymer will not be lost, it is desirable.

[2027]Also in such a leaving group content alkanyl compound, for the reason reactivity is high. VCM/PVC, vinyl bromide, iodination vinyl, isopropenyl chloride, isopropenyl bromide, iodination isopropenyl, an allyl chloride, an allyl bromide, allyl iodide, a 3-chloro-1-butene, a 3-bromo-1-butene, a 3-iodo-1-butene, a 3-chloro-2-methyl-1-propene, A 3-bromo-2-methyl-1-propene, a 3-iodo-2-methyl-1-propene, Allyl acetate, a 3-acetoxy 1-butene, a 3-acetoxy 2-methyl-1-propene, Chlorination-4-vinylbenzyl and-4-allylbenzyl chloride, bromination-4-vinylbenzyl, and-4-allylbenzyl bromide is preferred, and an allyl chloride, an allyl bromide, and especially allyl acetate are preferred at the point that acquisition is still easier.

[0028] To halogen of the end of the formula 1, make a metal simple substance or an organic metallic compound act, and it metal-izes. In the manufacturing method of the acrylic polymer which has an alkenyl group at the end (meta) making an alkenyl group content electrophilicity compound react furthermore, The combination of a desirable reacting agent is using the above alkenyl group content compounds which have a leaving group as an electrophilicity compound, using zinc as metal. In order to advance this reaction more smoothly, various kinds of catalysts can be used. as such a catalyst—the copper compound (for example, a copper chloride.) of monovalence A copper bromide, the copper compound (for example, copper acetylacetonato) of bivalence, zerovalent Ni compounds. They are (for example, tetrakis triphenyl phosphine nickel: $\text{Ni}(\text{PPh}_3)_4$), zerovalent Pd compound (for example, tetrakis(triphenyl phosphine)palladium— $\text{d}(\text{PPh}_3)_2$), etc.

[0029] As a method of introducing an alkenyl group into an end, the end of the acrylic polymer which has halogen at the end as shown in the general formula 1 (meta) is further changed into a hydroxyl content substituent, and the method of using the reactivity of hydroxyl after an appropriate time is mentioned. Various kinds of reactions can be used as a method of changing an end into a hydroxyl content substituent. For example, the acrylic polymer which has an end shown by the general formula 1 by the above-mentioned polymerizing method (meta) is manufactured. A method to which the compound is furthermore has a compound, and the alkenyl group and hydroxyl group of polymerization nature is made to react as the 2nd monomer. As opposed to the acrylic polymer which has a halogen end shown by the general formula 1 (meta), Make a metal simple substance or an organic metallo compound act, and halogen is metal-ized. They are the method of making it react to carbonyl compounds, such as aldehyde or ketone, the way alkali metal hydroxide like sodium hydroxide or a potassium hydrate replaces halogen directly, the way polyalcohol replaces halogen, etc.

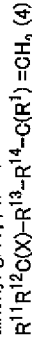
[0030] In addition to this as a method of introducing hydroxyl into an end, the halogenide which has a hydroxyl group by polymerization using the metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. The acrylic polymer which has halogen which has a hydroxyl group in one end and is shown in other ends by the formula 1 (meta) is manufactured. After an appropriate time, the method of changing into a hydroxyl group content substituent by the method which mentioned the halogen end above, and the method of carrying out coupling of the halogen ends using the compound which has a total of two or more same or different functional groups that can replace these halogen further are mentioned.

[0031] Thus, as a method of introducing an alkenyl group into the acrylic polymer which has a hydroxyl group at the obtained end (meta), for example, a method on which a base like an alkenyl group content halogenide like an allyl chloride and sodium methoxide is made to act, A method on which alkenyl group content isocyanate compounds, such as an allylisocyanate, are made to act, (Meta) The method of making alkenyl group content acid halide like acrylic acidchloride reacting under existence of bases, such as pyridine, the method of making alkenyl group content carboxylic acid like acrylic acid (meta) react under existence of a dehydration condensation catalyst, etc. are mentioned. [0032] In the manufacturing method of the acrylic polymer using the metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal for an organic halogenated compound or a sulfonyl halide compound as a catalyst

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi_eije?atw_u=http%3A%2F%2Fwww4.ipdl.i... 2010/03/03

(meta). If the organic halogenated compound which has an alkenyl group, or a sulfonyl halide compound is used as an initiator, the acrylic polymer which has an alkenyl group in an initiation terminal and in which a stop end has the structure of the formula 1 (meta) will be obtained. Thus, if halogen of the stop end of the polymer obtained is changed into an alkenyl group content substituent, the acrylic polymer which has an alkenyl group in both ends (meta) can be obtained.

[0033] Although there is no restriction in particular as an organic halogenated compound which has an alkenyl group, what has the structure shown in the general formula 4, for example is illustrated.



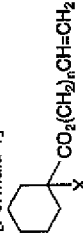
inside of formula, and R^1 — hydrogen or a methyl group, R^{11} and R^{12} — hydrogen. Or the univalent alkyl group of the carbon numbers 1–20, an aryl group, an alkyl or the thing mutually connected in the other end, and R^{13} — X in which C(O) O— (ester group), C(O) O— (keto group) or σ -, m -, p -phenylene group, and R^{14} may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1–20 is chlorine, bromine, or iodine.

The carbon which halogen has combined has combined with the carbonyl group or the phenyl group, a carbon-halogen bond is activated, and a polymerization starts these compounds.

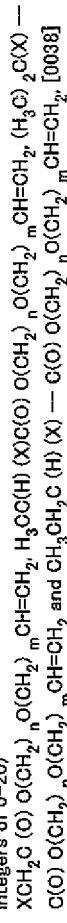
[0034] As an example of substituent R^{11} and R^{12} , hydrogen, a methyl group, an ethyl group, n -propyl group, an isopropyl group, n -butyl group, a pentyl group, a hexyl group, etc. are mentioned. In the other end, may connect R^{11} and R^{12} , they may form the annular skeleton, and, in such a case, R^{11} – R^{12} , for example, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, etc. are illustrated.

[0035] As an example of an organic halogenated compound shown by the general formula 4 of having an alkenyl group, $\text{XCH}_2\text{C}(\text{O})\text{OC}[\text{O}(\text{CH}_2)_n\text{CH}=\text{CH}_2 \text{ and } \text{H}_3]\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{O}(\text{CH}_2)_m\text{CH}=\text{CH}_2$, $(\text{H}_3\text{C})_2\text{C}(\text{X})-\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})-\text{C}(\text{O})\text{O}(\text{CH}_2)_m\text{CH}=\text{CH}_2$, [0036]

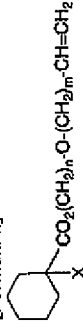
[Formula 1]



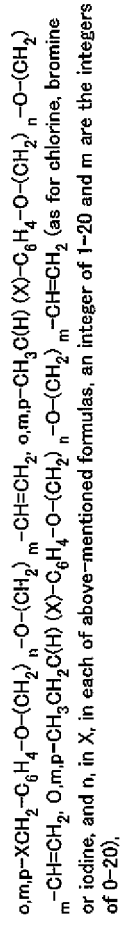
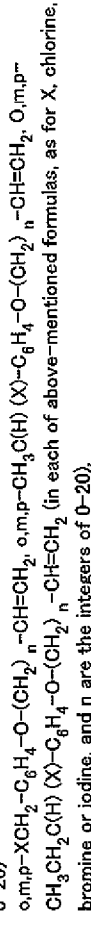
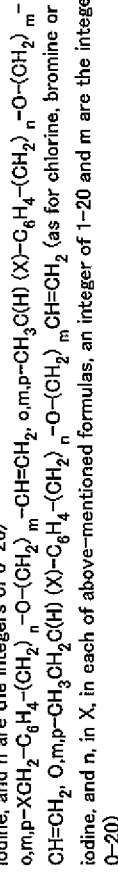
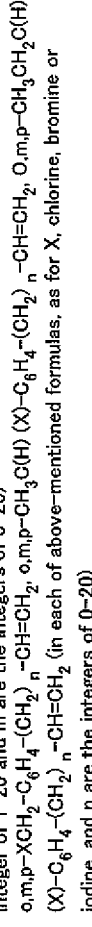
[0037] [In each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0–20]



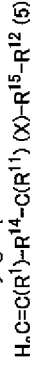
[Formula 2]



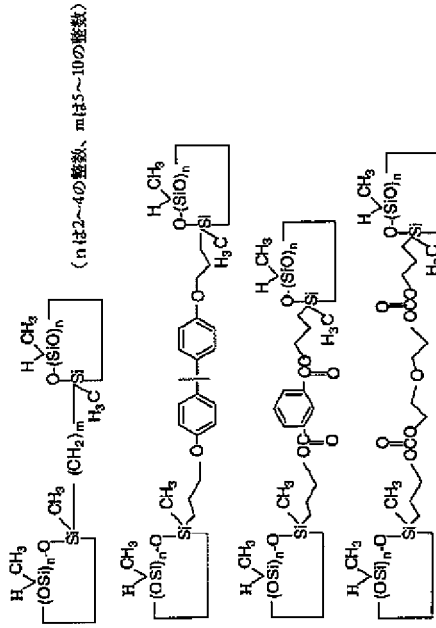
[0039] [As for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, the integer of 1–20 and m are the integers of 0–20]



A compound further shown by the general formula 5 as an organic halogenated compound which has an alkenyl group is mentioned.



(a formula — inside — R^{11} — R^{12} — R^{13} — R^{14} — R^{15} — R^{16} — R^{17} — R^{18} — R^{19} — R^{20} — R^{21} — R^{22} — R^{23} — R^{24} — R^{25} — R^{26} — R^{27} — R^{28} — R^{29} — R^{30} — R^{31} — R^{32} — R^{33} — R^{34} — R^{35} — R^{36} — R^{37} — R^{38} — R^{39} — R^{40} — R^{41} — R^{42} — R^{43} — R^{44} — R^{45} — R^{46} — R^{47} — R^{48} — R^{49} — R^{50} — R^{51} — R^{52} — R^{53} — R^{54} — R^{55} — R^{56} — R^{57} — R^{58} — R^{59} — R^{60} — R^{61} — R^{62} — R^{63} — R^{64} — R^{65} — R^{66} — R^{67} — R^{68} — R^{69} — R^{70} — R^{71} — R^{72} — R^{73} — R^{74} — R^{75} — R^{76} — R^{77} — R^{78} — R^{79} — R^{80} — R^{81} — R^{82} — R^{83} — R^{84} — R^{85} — R^{86} — R^{87} — R^{88} — R^{89} — R^{90} — R^{91} — R^{92} — R^{93} — R^{94} — R^{95} — R^{96} — R^{97} — R^{98} — R^{99} — R^{100} — R^{101} — R^{102} — R^{103} — R^{104} — R^{105} — R^{106} — R^{107} — R^{108} — R^{109} — R^{110} — R^{111} — R^{112} — R^{113} — R^{114} — R^{115} — R^{116} — R^{117} — R^{118} — R^{119} — R^{120} — R^{121} — R^{122} — R^{123} — R^{124} — R^{125} — R^{126} — R^{127} — R^{128} — R^{129} — R^{130} — R^{131} — R^{132} — R^{133} — R^{134} — R^{135} — R^{136} — R^{137} — R^{138} — R^{139} — R^{140} — R^{141} — R^{142} — R^{143} — R^{144} — R^{145} — R^{146} — R^{147} — R^{148} — R^{149} — R^{150} — R^{151} — R^{152} — R^{153} — R^{154} — R^{155} — R^{156} — R^{157} — R^{158} — R^{159} — R^{160} — R^{161} — R^{162} — R^{163} — R^{164} — R^{165} — R^{166} — R^{167} — R^{168} — R^{169} — R^{170} — R^{171} — R^{172} — R^{173} — R^{174} — R^{175} — R^{176} — R^{177} — R^{178} — R^{179} — R^{180} — R^{181} — R^{182} — R^{183} — R^{184} — R^{185} — R^{186} — R^{187} — R^{188} — R^{189} — R^{190} — R^{191} — R^{192} — R^{193} — R^{194} — R^{195} — R^{196} — R^{197} — R^{198} — R^{199} — R^{200} — R^{201} — R^{202} — R^{203} — R^{204} — R^{205} — R^{206} — R^{207} — R^{208} — R^{209} — R^{210} — R^{211} — R^{212} — R^{213} — R^{214} — R^{215} — R^{216} — R^{217} — R^{218} — R^{219} — R^{220} — R^{221} — R^{222} — R^{223} — R^{224} — R^{225} — R^{226} — R^{227} — R^{228} — R^{229} — R^{230} — R^{231} — R^{232} — R^{233} — R^{234} — R^{235} — R^{236} — R^{237} — R^{238} — R^{239} — R^{240} — R^{241} — R^{242} — R^{243} — R^{244} — R^{245} — R^{246} — R^{247} — R^{248} — R^{249} — R^{250} — R^{251} — R^{252} — R^{253} — R^{254} — R^{255} — R^{256} — R^{257} — R^{258} — R^{259} — R^{260} — R^{261} — R^{262} — R^{263} — R^{264} — R^{265} — R^{266} — R^{267} — R^{268} — R^{269} — R^{270} — R^{271} — R^{272} — R^{273} — R^{274} — R^{275} — R^{276} — R^{277} — R^{278} — R^{279} — R^{280} — R^{281} — R^{282} — R^{283} — R^{284} — R^{285} — R^{286} — R^{287} — R^{288} — R^{289} — R^{290} — R^{291} — R^{292} — R^{293} — R^{294} — R^{295} — R^{296} — R^{297} — R^{298} — R^{299} — R^{300} — R^{301} — R^{302} — R^{303} — R^{304} — R^{305} — R^{306} — R^{307} — R^{308} — R^{309} — R^{310} — R^{311} — R^{312} — R^{313} — R^{314} — R^{315} — R^{316} — R^{317} — R^{318} — R^{319} — R^{320} — R^{321} — R^{322} — R^{323} — R^{324} — R^{325} — R^{326} — R^{327} — R^{328} — R^{329} — R^{330} — R^{331} — R^{332} — R^{333} — R^{334} — R^{335} — R^{336} — R^{337} — R^{338} — R^{339} — R^{340} — R^{341} — R^{342} — R^{343} — R^{344} — R^{345} — R^{346} — R^{347} — R^{348} — R^{349} — R^{350} — R^{351} — R^{352} — R^{353} — R^{354} — R^{355} — R^{356} — R^{357} — R^{358} — R^{359} — R^{360} — R^{361} — R^{362} — R^{363} — R^{364} — R^{365} — R^{366} — R^{367} — R^{368} — R^{369} — R^{370} — R^{371} — R^{372} — R^{373} — R^{374} — R^{375} — R^{376} — R^{377} — R^{378} — R^{379} — R^{380} — R^{381} — R^{382} — R^{383} — R^{384} — R^{385} — R^{386} — R^{387} — R^{388} — R^{389} — R^{390} — R^{391} — R^{392} — R^{393} — R^{394} — R^{395} — R^{396} — R^{397} — R^{398} — R^{399} — R^{400} — R^{401} — R^{402} — R^{403} — R^{404} — R^{405} — R^{406} — R^{407} — R^{408} — R^{409} — R^{410} — R^{411} — R^{412} — R^{413} — R^{414} — R^{415} — R^{416} — R^{417} — R^{418} — R^{419} — R^{420} — R^{421} — R^{422} — R^{423} — R^{424} — R^{425} — R^{426} — R^{427} — R^{428} — R^{429} — R^{430} — R^{431} — R^{432} — R^{433} — R^{434} — R^{435} — R^{436} — R^{437} — R^{438} — R^{439} — R^{440} — R^{441} — R^{442} — R^{443} — R^{444} — R^{445} — R^{446} — R^{447} — R^{448} — R^{449} — R^{450} — R^{451} — R^{452} — R^{453} — R^{454} — R^{455} — R^{456} — R^{457} — R^{458} — R^{459} — R^{460} — R^{461} — R^{462} — R^{463} — R^{464} — R^{465} — R^{466} — R^{467} — R^{468} — R^{469} — R^{470} — R^{471} — R^{472} — R^{473} — R^{474} — R^{475} — R^{476} — R^{477} — R^{478} — R^{479} — R^{480} — R^{481} — R^{482} — R^{483} — R^{484} — R^{485} — R^{486} — R^{487} — R^{488} — R^{489} — R^{490} — R^{491} — R^{492} — R^{493} — R^{494} — R^{495} — R^{496} — R^{497} — R^{498} — R^{499} — R^{500} — R^{501} — R^{502} — R^{503} — R^{504} — R^{505} — R^{506} — R^{507} — R^{508} — R^{509} — R^{510} — R^{511} — R^{512} — R^{513} — R^{514} — R^{515} — R^{516} — R^{517} — R^{518} — R^{519} — R^{520} — R^{521} — R^{522} — R^{523} — R^{524} — R^{525} — R^{526} — R^{527} — R^{528} — R^{529} — R^{530} — R^{531} — R^{532} — R^{533} — R^{534} — R^{535} — R^{536} — R^{537} — R^{538} — R^{539} — R^{540} — R^{541} — R^{542} — R^{543} — R^{544} — R^{545} — R^{546} — R^{547} — R^{548} — R^{549} — R^{550} — R^{551} — R^{552} — R^{553} — R^{554} — R^{555} — R^{556} — R^{557} — R^{558} — R^{559} — R^{560} — R^{561} — R^{562} — R^{563} — R^{564} — R^{565} — R^{566} — R^{567} — R^{568} — R^{569} — R^{570} — R^{571} — R^{572} — R^{573} — R^{574} — R^{575} — R^{576} — R^{577} — R^{578} — R^{579} — R^{580} — R^{581} — R^{582} — R^{583} — R^{584} — R^{585} — R^{586} — R^{587} — R^{588} — R^{589} — R^{590} — R^{591} — R^{592} — R^{593} — R^{594} — R^{595} — R^{596} — R^{597} — R^{598} — R^{599} — R^{600} — R^{601} — R^{602} — R^{603} — R^{604} — R^{605} — R^{606} — R^{607} — R^{608} — R^{609} — R^{610} — R^{611} — R^{612} — R^{613} — R^{614} — R^{615} — R^{616} — R^{617} — R^{618} — R^{619} — R^{620} — R^{621} — R^{622} — R^{623} — R^{624} — R^{625} — R^{626} — R^{627} — R^{628} — R^{629} — R^{630} — R^{631} — R^{632} — R^{633} — R^{634} — R^{635} — R^{636} — R^{637} — R^{638} — R^{639} — R^{640} — R^{641} — R^{642} — R^{643} — R^{644} — R^{645} — R^{646} — R^{647} — R^{648} — R^{649} — R^{650} — R^{651} — R^{652} — R^{653} — R^{654} — R^{655} — R^{656} — R^{657} — R^{658} — R^{659} — R^{660} — R^{661} — R^{662} — R^{663} — R^{664} — R^{665} — R^{666} — R^{667} — R^{668} — R^{669} — R^{670} — R^{671} — R^{672} — R^{673} — R^{674} — R^{675} — R^{676} — R^{677} — R^{678} — R^{679} — R^{680} — R^{681} — R^{682} — R^{683} — R^{684} — R^{685} — R^{686} — R^{687} — R^{688} — R^{689} — R^{690} — R^{691} — R^{692} — R^{693} — R^{694} — R^{695} — R^{696} — R^{697} — R^{698} — R^{699} — R^{700} — R^{701} — R^{702} — R^{703} — R^{704} — R^{705} — R^{706} — R^{707} — R^{708} — R^{709} — R^{710} — R^{711} — R^{712} — R^{713} — R^{714} — R^{715} — R^{716} — R^{717} — R^{718} — R^{719} — R^{720} — R^{721} — R^{722} — R^{723} — R^{724} — R^{725} — R^{726} — R^{727} — R^{728} — R^{729} — R^{730} — R^{731} — R^{732} — R^{733} — R^{734} — R^{735} — R^{736} — R^{737} — R^{738} — R^{739} — R^{740} — R^{741} — R^{742} — R^{743} — R^{744} — R^{745} — R^{746} — R^{747} — R^{748} — R^{749} — R^{750} — R^{751} — R^{752} — R^{753} — R^{754} — R^{755} — R^{756} — R^{757} — R^{758} — R^{759} — R^{760} — R^{761} — R^{762} — R^{763} — R^{764} — R^{765} — R^{766} — R^{767} — R^{768} — R^{769} — R^{770} — R^{771} — R^{772} — R^{773} — R^{774} — R^{775} — R^{776} — R^{777} — R^{778} — R^{779} — R^{780} — R^{781} — R^{782} — R^{783} — R^{784} — R^{785} — R^{786} — R^{787} — R^{788} — R^{789} — R^{790} — R^{791} — R^{792} — R^{793} — R^{794} — R^{795} — R^{796} — R^{797} — R^{798} — R^{799} — R^{800} — R^{801} — R^{802} — R^{803} — R^{804} — R^{805} — R^{806} — R^{807} — R^{808} — R^{809} — R^{810} — R^{811} — R^{812} — R^{813} — R^{814} — R^{815} — R^{816} — R^{817} — R^{818} — R^{819} — R^{820} — R^{821} — R^{822} — R^{823} — R^{824} — R^{825} — R^{826} — R^{827} —



[0054] Although a polymer (A) and a hardening agent (B) are mixable at an arbitrary rate, it is preferred that the mole ratio of an alkenyl group and a hydrosilyl group is in the range of 5-0.2 from the field of hardenability, and it is still more preferred that it is especially 2.5-0.4. If smaller [if a mole ratio becomes five or more, only a hardened material with insufficient hardening and small intensity with stickiness will be obtained, and] than 0.2, since a hydrosilyl group [activity / in a hardened material / after / hardening] remains in large quantities, a crack and a void occur, it will be uniform and a hardened material with intensity will not be obtained.

[0055] Although a hardening reaction of a polymer (A) and a hardening agent (B) advances by mixing and heating two ingredients, a hydrosilylation catalyst is added in order to advance a reaction more nearly promptly. As such a hydrosilylation catalyst, radical initiators, such as organic peroxide and an azo compound, and a transition metal catalyst are mentioned. As a radical initiator, there is no restriction in particular and various kinds of things can be used. If it illustrates, di-*t*-butylperoxide, 2,5-dimethyl-2,5-di-*t*-butylperoxy hexane, 2,5-dimethyl-2,5-di-*t*-butylperoxy-3-hexene, Dialkyl peroxide like dicumyl peroxide, *t*-butyl cumyl peroxide, alpha, and alpha-bis(*t*-butylperoxy) isopropylbenzene, Benzoyl peroxide, *p*-chlorobenzoyl peroxide, *m*-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, diacylperoxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic acid-*t*-butyl, fault-Jl diisopropyl carbonate, Peroxyketal like peroxy dicarbonate like fault-Jl di-carbonate 2-ethylhexyl, 1,1-di-*t*-butylperoxy cyclohexane, and 1,1-di-*t*-butylperoxy-3,3,5-trimethylcyclohexane, etc. are mentioned.

[0056] As a transition metal catalyst, for example A platinum simple substance, alumina, silica, A complex with a thing which made carriers, such as carbon black, distribute a platinum solid, chloroplatinic acid, chloroplatinic acid, alcohol, aldehyde, ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhCl(PPh₃)₃, RhCl₃, RuCl₃, IrCl₃, FeCl₃, AlCl₃, PdCl₂-H₂O, NiCl₂, TiCl₄, etc. are mentioned. These catalysts may be used independently, and even if they use two or more kinds together, they are not cared about. Although there is no restriction in particular as a catalyst amount, it is good to use in the range of 10⁻³ - 10⁻⁶ mol to 1 mol of alkenyl groups of the (A) ingredient often [using in the range of 10⁻¹ - 10⁻⁸ mol], and preferably, if less than 10⁻⁶ mol, hardening will not fully advance. Since a hydrosilylation catalyst is expensive, it is preferred that more than 10⁻¹ mol does not use.

[0057] A uniform hardened material excellent in depths hardenability is obtained without being accompanied by phenomena, such as foaming, if a hydrosilylation catalyst is mixed and stiffened [two ingredients (A), (B), and if needed]

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web_ogi_eje?atw_u=http%3A%2F%2Fwww4.ipdl... 2010/03/03

for this invention. Although there is no restriction in particular about curing conditions, generally it is good to harden [0 ** - 200 **] at 30 ** - 150 ** preferably for 10 seconds - 24 hours. At an elevated temperature (80 ** - 150 **), what is hardened in a short time of 10 seconds - about 1 hour is obtained especially. Description of a hardened material can be broadly created from a rubber-like thing to a resin-like thing, although it is dependent on a principal chain skeleton and a molecular weight of a polymer of the (A) ingredient to be used, and a hardening agent of the (B) ingredient. If a concrete use of a hardened material obtained from this constituent is mentioned, they will be a sealing material, adhesives, an adhesive material, elastic adhesives, a paint, powder coatings, foam, a potting material for electric electrons, a film, a gasket, various molding materials, artificial marble, etc.

[0058] An acrylic polymer which has crosslinkable silyl groups at the end of this invention (meta). Like a manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It can obtain by changing halogen of an acrylic polymer which has halogen (meta) into an end which is obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst and which shows by the general formula 1.

[0059] As such a converting method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has terminal structures which show the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements in the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. A method to which a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature is made to react as the 2nd monomer is mentioned. This method is based on the same principle as a method illustrated in a manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta). After the 1st polymerization ends the 2nd monomer and isolating a polymer also in this case, it may add with a catalyst and may be made to newly react, and it may add in the middle of a polymerization (inch-situ), and may be made to react. In the case of the latter, a monomer inversion rate of the 1st polymerization is so good that it is high, and is not less than 80% preferably. Crosslinkable silyl groups will be distributed over a side chain instead of a molecular terminal as it is 80% or less, and the mechanical characteristic of a hardened material will be spoiled. If a compound which has an alkenyl group and crosslinkable silyl groups of such polymerization nature is added in equivalent amount to the number of whole ends, crosslinkable silyl groups will be theoretically introduced into all the ends, but in order to introduce a cross-linking group into a whole end certainly, specifically, it is good to use one to 5 times to the number of ends in excessive amount. If it uses 5 or more times, a cross-linking group will be introduced into an end of a polymer by high density, and it is not desirable on hardened material physical properties.

[0060] Although there is no restriction in particular as a compound which combines and has such an alkenyl group and crosslinkable silyl groups of polymerization nature, if it illustrates concretely, general formula 6H₂C=O(R³)-R⁴-R⁵-[Si(R¹⁶)₂-b(Y)₆O]₃-m-Si(R¹⁷)₃-a(O)₃ (R², R⁴, and R⁵ among a formula) R³ in the general formula 2, R⁴, and R⁵ - the same - R¹⁶ and R¹⁷. All an alkyl group of the carbon numbers 1-20, an aryl group, an aralkyl group, Or (R¹)₃SiO - (R¹) is a univalent hydrocarbon group of the carbon numbers 1-20, and) times R¹ being the same and differing - **** - when the Tori ORGANO siloxy group shown is shown and R¹⁶ or two or more R¹⁷ exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydroxylic basis and two or more Y exists, they may be the same and may differ, a shows 0, 1, 2, or 3, and b shows 0, 1, or 2, m is an integer of 0-19. However, it shall satisfy that it is a+m-b>=1. A compound shown is mentioned. When R⁴ is -C(O)O- (ester group), it is a compound of an acrylate (meta) system, and when R⁴ is a phenylene group, it is a compound of a styrene system.

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web_ogi_eje?atw_u=http%3A%2F%2Fwww4.ipdl... 2010/03/03

brine (10mL) further. The organic layer was dried by Na_2SO_4 , and volatile matter content was decompression-ization-distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the allyloxy ethyl-2-bromopropionate shown in a lower type was obtained. (78.5-81 ° (1.3mmHg), 2.986g).

[0090] $\text{CH}_3\text{C}(\text{H})(\text{Br})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}=\text{CH}_2$ [0091]

[The example 3 of manufacture]

(Manufacture 2 of the organic halogenated compound which has an alkenyl group) The nitrogen purge of the two-lot flask of 50mL was carried out, and a 5-hexen-1-ol (2.81mL, 23.4mmol), pyridine (3mL), and THF (10mL) were taught. The solution was cooled at 0 ° and 2-bromo propionyl chloride (2mL, 19.52mmol) was dropped slowly. After continuing churning at a temperature as it is for 1 hour, filtration removed the hydrochloride of the pyridine which added and generated ethyl acetate (10mL). Filtrate — dilute hydrochloric acid (10mL) and NaHCO_3 solution (10mL) — it washed by brine (10mL) further. The organic layer was dried by Na_2SO_4 , and volatile matter content was decompression-ization-distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the hexenyl-2-bromopropionate shown in a lower type was obtained. (82-83 ° (2.3mmHg), 3.101g).

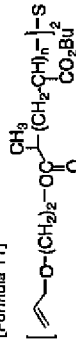
$\text{CH}_3\text{C}(\text{H})(\text{Br})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CH}_2-\text{CH}=\text{CH}_2$ [0092]

[Work example 6] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (2.5 mL). The initiator which has the alkenyl group obtained in 2.24 g, 17.45mmol, and the example 2 of manufacture (165 mg) 0.698mmol, the first copper (100 mg, 0.698mmol) of bromination, a 2,2'-bipyridyl (218 mg, 1.40mmol), acetonitrile (0.5mL), and ethyl acetate (2mL) were prepared, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ° and made to react for 50 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4 , volatile matter content was distilled off under decompression, and 1.90g of poly (butyl acrylate) which has bromine was obtained in an alkenyl group and other ends to one end (79%). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 3600, and molecular weight distribution was 1.51. The number of the alkenyl groups introduced per one molecule of oligomer was 0.75 from ^1H NMR analysis.

[0093] Next, the polymer (1.90g) produced by 3 mouth flask of 50mL provided with the stirring bar and the flowing-back condenser tube by performing it above, $\text{Na}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$ (70.2 mg, 0.293mmol), and ethanol (3mL) were taught, and it agitated at flowing-back temperature for 3 hours. After cooling to a room temperature, ethyl acetate (10mL) and dilute hydrochloric acid (10mL) were added, and it separated two-layer. After washing the organic layer by dilute hydrochloric acid and brine and drying by Na_2SO_4 , 1.69g of poly(acrylic acid) butyl which has an alkenyl group in the both ends shown in a lower type was obtained by distilling off volatile matter content under decompression. In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

[0094]

[Formula 11]



[0095]

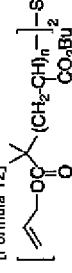
[Work example 7] To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2-

methyl-2-bromopropionic acid allyl (0.354 mL) 460 mg, 2.22mmol, the first copper (318 mg, 2.22mmol) of bromination, a 2,2'-bipyridyl (1.04 g, 8.66mmol), acetonitrile (1mL), and ethyl acetate (4mL) were prepared, and the sealed tube was carried out, after performing the vacuum desiring 3 times and removing dissolved oxygen. The mixture was heated at 80 ° and made to react for 3 hours. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4 , volatile matter content was distilled off under decompression, and 3.93g of poly (butyl acrylate) which has bromine was obtained in an alkenyl group and other ends to one end (75%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 2700, and molecular weight distribution was 1.48. The number of the alkenyl groups introduced per one molecule of oligomer was 0.81 from ^1H NMR analysis.

[0096] Next, the polymer (1.17g) produced by 3 mouth flask of 50mL provided with the stirring bar and the flowing-back condenser tube by performing it above, $\text{Na}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$ (57.6 mg, 0.240mmol), and ethanol (2mL) were taught, and it agitated at flowing-back temperature for 3 hours. After cooling to a room temperature, ethyl acetate (10mL) and dilute hydrochloric acid (10mL) were added, and it separated two-layer. After washing the organic layer by dilute hydrochloric acid and brine and drying by Na_2SO_4 , 1.11g of poly(acrylic acid) butyl which has an alkenyl group in the both ends shown in a lower type was obtained by distilling off volatile matter content under decompression. In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 4200, and molecular weight distribution was 1.71.

[0097]

[Formula 12]

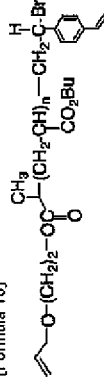


[0098]

[Work example 8] To the resisting pressure glass reaction vessel of 100mL, it is butyl acrylate (10 mL). The initiator which has the alkenyl group obtained in 8.94 g, 69.8mmol, and the example 2 of manufacture (332 mg) 1.40mmol, the first copper (200 mg, 1.40mmol) of bromination, a 2,2'-bipyridyl (433 mg, 2.80mmol), acetonitrile (2mL), and ethyl acetate (8mL) were prepared, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ° and made to react for 1.5 hours. After cooling to a room temperature, the sealed tube of the p-divinylbenzene (364 mg, 2.80mmol) was added and carried out under a nitrogen gas atmosphere. The mixture was heated at 100 ° and made to react for 2 hours. After diluting the mixture with ethyl acetate (30mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4 , volatile matter content was distilled off under decompression, and 6.43g of poly(butyl acrylate) which has an alkenyl group in the both ends shown in a lower type was obtained (69%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 3800, and molecular weight distribution was 5.35. The number of the alkenyl groups introduced per one molecule of oligomer was 1.73 from ^1H NMR analysis.

[0099]

[Formula 13]



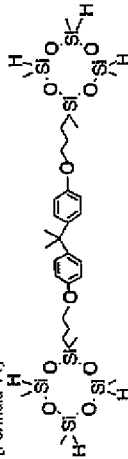
[0100]

[Examples 9-14] The polymer which has an alkenyl group in the both ends obtained in creation examples 1, 2, 3, 6, 7, and 8 of the hardened material was dissolved in toluene, and a polymer and equivalent weight of silicic acid aluminum (the product made from harmony chemicals: KYO word 700PEL) were added. It agitated for 1 hour, and the minute impurities in a polymer were removed. Next, 1, 1 and 3 of the multivalent hydrogen silicon compound shown in a lower type and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex (8.3x10⁻⁸ mol/L xylene solution) were well mixed with the refined poly (acrylic ester). The quantity from which, as for the amount of the multivalent hydrogen silicon compound used, the alkenyl group of a polymer and the hydrosilyl group of a hydrogen silicon compound will be 1/1.2 by a mole ratio, and the amount of the platinum catalyst used were made into the 10⁻⁴ - 10⁻³ equivalent by the mole ratio to the alkenyl group of a polymer.

[0101] Thus, the hardening examination was done on a 130 °C hot plate for some obtained constituents, and gel time was measured. It deaerated under decompression of the remaining constituents, heat cure was slushed and carried out to the mold, and the rubber-like hardened material was obtained. The hardened material was immersed in toluene for 24 hours, and the gel fraction was measured from weight changes in front and behind. The result was shown in Table 1.

[0102]

[Formula 14]



[0103]

[Table 1]

実施例	重合体	白金触媒の含有率 (モル%)	30℃に於けるゲル化時間	硬化物の形成条件	硬化物のゲル化率 (%)
実施例 9	重合体 1	1.0**	3分	100℃ 15時間	61
実施例 10	重合体 2	1.0**	45秒	100℃ 17時間	35
実施例 11	重合体 3	1.0**	1分40秒	100℃ 8時間	77
実施例 12	重合体 0	1.0**	4分	100℃ 18時間	77
実施例 13	重合体 7	1.0**	2分	100℃ 15時間	40
実施例 14	重合体 8	1.0**	11秒	103℃ 12時間	84

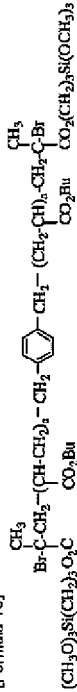
[0104]

[Work example 15] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL), 34.9mmol, alpha, and alpha'-dibromo-p-xylene (185 mg) 0.70mmol, the first copper (100 mg, 0.70mmol) of bromination, a 2,2'-bipyridyl (1.09 g, 7.0mmol), and acetonitrile (5mL) were taught, and the sealed tube was carried out, after performing vacuum devolatilization 3 times and removing dissolved oxygen. The mixture was heated at 130 °C and made to react for 6 hours. After diluting the mixture with ethyl acetate (mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine 3 times. The organic layer was dried by Na₂SO₄; volatile matter content was distilled off under decompression, and the poly (butyl acrylate) which has bromine in both ends was obtained (3.04 g, 68% of

polymerization yield). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 5200, and molecular weight distribution was 1.17. Next, the poly (butyl acrylate) (1g) which has bromine in the both ends obtained by the resisting pressure coil of 30mL in the top. Trimethoxysilylpropyl methacrylate (285 mg, 1.15mmol). When copper (27.6 mg, 0.103mmol), a 2,2'-bipyridyl (300 mg, 1.93mmol), and ethyl acetate (3mL) were prepared for a start [bromination] and it was made to react at 130 °C for 6 hours, the poly (butyl acrylate) which has a trimethoxysilyl group at the end shown in a lower type was obtained.

[0105]

[Formula 15]



[0106]

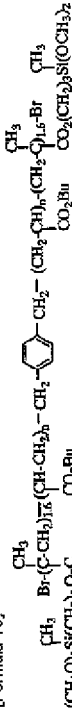
[Work example 16] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL), 34.9mmol, alpha, and alpha'-dibromo-p-xylene (185 mg) 0.70mmol, the first copper (100 mg, 0.70mmol) of bromination, a 2,2'-bipyridyl (217 mg, 1.40mmol), ethyl acetate (4mL), and acetonitrile (1mL) were taught, and the sealed tube was carried out, after performing nitrogen bubbling for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 °C and made to react for 2 hours. After cooling a mixture, methyl dimethoxy silyl propyl methacrylate (650 mg, 2.8mmol) was added, and it was made to react at 100 °C for 2 hours. After diluting with ethyl acetate (20mL) after cooling a mixture and filtering the generated insoluble solid, ammonium chloride solution washed filtrate once by brine twice. The organic layer was dried by Na₂SO₄; volatile matter content was distilled off under decompression, and 4.78g of poly (butyl acrylate)

which has a methyl dimethoxy silyl group in the both ends shown in a lower type was obtained (80%). By GPC

measurement (polystyrene conversion), the number average molecular weight of the polymer was 7100, and molecular weight distribution was 1.74. The number of the silyl groups introduced per monad by ¹HNMR analysis was 3.2.

[0107]

[Formula 16]



[0108] Next, poly (butyl acrylate) (2.5g) and the curing catalyst (Japanese East transformation make, U-220 or 75 mg) which have crosslinkable silyl groups in the both ends produced by performing it above were mixed well, and it slushed into the mold, and defoamed at the room temperature using decompression oven. The uniform rubber-like hardened material was obtained by neglecting it for seven days to a room temperature. The gel fraction was 54%.

[0109]

[Effect of the Invention] In this invention, the acrylic (meta) polymer in which manufacturing until now has an alkenyl group or a hydroxylic silyl group by a high ratio at the difficult end can be obtained simple, and those functional groups are certainly introduced into the end.

Therefore, the hardened material which was excellent in the hardening characteristic can be obtained.

[Translation done.]